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KINETICS OF SINTERING CHROMIUM CARBIDE

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SUMMARY

The sintering of chromium carbide under pressure was investigated in order to study the kinetics of grain growth and densification during this process. The results indicated that the grain diameter D and sintering time t can be related by the expression $D^n = Kt$ where K is a rate constant. The value of n was associated with the location, size, and shape of the pores in the compact.

Densification of a sintered chromium carbide compact was accompanied by grain growth, and density and grain size seem to be interdependent during this stage of the sintering process. Grain growth continued after densification was complete, and for this stage, an activation energy for grain growth was obtained.

INTRODUCTION

Sintering is a process of technological importance in the powdered metals, carbide, glass, and ceramic industries. An understanding of the mechanism and kinetics of sintering should assist in the commercial fabrication of materials having optimum properties. Sintering can occur because a mass of powder has excess free energy over the same mass in a densified state because of the higher total surface area of the powder. Powders may be sintered with or without the presence of a liquid phase. The present investigation conducted at the NACA Lewis laboratory deals with the sintering of chromium carbide at temperatures below its melting point.

This dry sintering process is conveniently divided into two stages by Shaler (reference 1): the first stage, during which the particles preserve much of their original shape and the voids are interconnected, and the second stage, during which densification occurs and the pores are isolated. The investigation by Kuczynski (reference 2) indicates that the mechanism of forming interfaces between particles, or welding together of particles during the first stage of sintering, may be described by any one or a combination of the following mechanisms: viscous flow, evaporation and condensation, volume diffusion, or surface diffusion.

The mechanism by which the pores are closed or eliminated during the second stage of sintering is of interest. Grain growth, another process which has been previously observed during this stage, may be attributed to the variation in the surface energies of the individual grains, causing some grains to grow at the expense of others. Grain growth occurs by grain-boundary migration, which presumably requires diffusion and, therefore, the rate of grain growth would be expected to increase exponentially with increasing temperature. For practical sintering times of less than 1 hour, a certain minimum temperature may exist at which major structural and property changes will occur.

Sintering under pressure (hot pressing) is a commercial process during which heat and pressure are applied to the compact simultaneously. The kinetics of grain growth and densification during the sintering under pressure of a carbide were investigated to provide additional information which will aid in describing more accurately the mechanisms involved. Chromium carbide Cr_3C_2 was used because it is resistant to oxidation and is stable at elevated temperature. In addition, this material may be sintered at relatively low temperatures and therefore is convenient to use for this type of investigation. Specimens for study were prepared by sintering under pressure at different temperatures and for various periods of time.

APPARATUS AND PROCEDURE

Material. - The chromium carbide powder used in this investigation was obtained commercially. An X-ray diffraction powder pattern showed the characteristic lines of Cr_3C_2 . The calculated percentages by weight and the chemical analysis of the powder are presented in the following table:

	Calculated weight (percent)	Chemical analysis (percent)
Chromium	86.6	86.19
Carbon	13.4	12.14
Iron	----	.20

Initial particle-size measurements. - The size of the powder particles were measured with a microscope having a calibrated filar eyepiece. The powder particles were distributed uniformly on several glass slides with water as the dispersing agent. Particles were measured on different parts of the slides in order to obtain a representative sample. The average initial particle size was found to be 6.0 microns and 85 percent of the particles were between 2 and 10 microns.

Sintering. - Specimens were prepared by sintering under pressure. Graphite dies (reference 3) heated by induction were used to form the specimens. Sintering temperatures were measured with an optical pyrometer by sighting between two adjacent loops of the induction coil into a 3/8-inch-diameter hole that was drilled 1 inch deep into the graphite die at the midsection. The maximum temperature variation of the specimen was $\pm 5.5^{\circ}\text{C}$ ($\pm 10^{\circ}\text{F}$). A load was applied to the specimen through a lever system which had a ratio of 24.

Each sample consisted of 80 grams of chromium carbide powder, which was placed in the specimen chamber ($1\frac{13}{16}$ -in. diam.) of the graphite die. A load of approximately 1 ton per square inch was applied to the powder by means of the lever system described previously. The die and specimen were heated in 20 minutes to the highest temperature (2500°F) at which no increase in grain size could be observed. The time required to heat from this temperature to the maximum temperature (3000°F) used in this investigation was less than 2.5 minutes. Specimens used in this investigation were sintered at the temperatures and times indicated in table I.

Grain-size measurements. - Samples were mounted in bakelite and polished with diamond abrasives in preparation for grain-size measurements. The etchant used to reveal the grain boundaries was a 1:1 mixture of 20-percent potassium hydroxide and 20-percent potassium ferricyanide heated to 160°F . Representative areas of the sample were photographed at 1000 diameters. The largest diameters of all well-defined grains were measured, but only the measurements of 15 of the largest grains were averaged in order to determine the grain growth. The largest grains of each sample were used on the assumption that they were among the first to begin growth.

Density. - Density measurements for this investigation were made by differential weighing of samples in air and water. An analytical balance was used, and the individual values are considered correct within ± 0.01 gram per milliliter.

RESULTS AND DISCUSSION

Grain growth has been observed in metal compacts sintered at a temperature which was about two-thirds of the absolute temperature of the melting point (reference 4). Grain growth also occurs during the sintering of chromium carbide and is illustrated by the series of photomicrographs shown in figures 1 and 2. Specimens shown in figure 1 were prepared by sintering for 90 minutes at temperatures ranging from 1371°C (2500°F) to 1648°C (3000°F). Photomicrographs which show the increase in grain size with sintering time at 1538°C (2800°F) for chromium carbide compacts are shown in figure 2. Table I presents the

average grain-size measurements and the density of the specimens prepared for this investigation. Figure 3 shows the relation between the grain-size measurements of the samples shown in figure 1 and sintering temperature.

Grain growth in polycrystalline solids and in sintered bodies may occur from grain-boundary migration which results in the gradual absorption of some grains by others. During the sintering of a mass of polycrystalline nonductile particles, grain growth probably occurs first within the boundaries of the particles. This internal grain growth (that is, within the particles) is assumed to be of little importance in sintering (reference 5). Grain-boundary migration across the particle boundary begins after sintering has proceeded to the point at which substantial bonds which permit absorption of one grain by another, have been formed between the particles.

Beck investigated the kinetics of grain growth in brass and expressed grain growth by an empirical equation (reference 6). In order to determine if grain growth observed during the sintering of a mass of powders can be expressed similarly, the logarithm of the average measured grain size of the specimens was plotted against logarithm of time for constant sintering temperature (fig. 4). Two groups of parallel lines appear and the relation between grain size and sintering time for each group can be expressed by the empirical equation:

$$D^n = Kt \quad (1)$$

where

- D average measured grain size, microns
- K rate constant (function of temperature and n)
- n constant for each group
- t sintering time, minutes

In the lower temperature range between 1371° and 1482° C (2500° and 2700° F) for the time periods investigated, n is 10. For the higher temperature range of this investigation between 1538° and 1628° C (2800° and 3000° F), n is 6. It will be shown later that the values of n may be associated with different stages of the sintering process.

The different slopes $1/n$ indicate that a change occurs in the sintering process. Photographs in figure 1 indicate that where n is 10 (for sintering time periods of 90 min), most of the pores are located

in the grain boundaries, and that with increasing temperature, the number and size of pores decrease (density increases) while grain growth occurs. Where n is 6, figure 1 shows that (for specimens sintered for 90 min) the pores have spheroidized and tend to be located within the grains as temperature increases. Photographs of specimens sintered for other periods of time show the same tendencies. When the pores become spheroidized, most of the pore volume has been eliminated and further sintering does not yield an appreciable increase in density. After the remaining pores become located within the grains, the mechanism of their elimination is probably self-diffusion, which is a relatively slow process.

In agreement with the foregoing discussion, the measured densities of specimens sintered for 90 minutes at various sintering temperatures (fig. 5) show that there is a large increase in density when n is 10 and that when n becomes 6 no appreciable increase in density is observed. It might be hypothesized that for longer sintering times (in excess of 90 min) in the range where n is 10, the pores will tend to spheroidize and to be located within the grains as they do for shorter times where n is 6, and a corresponding change in $1/n$ (slope) would be expected.

In order to better illustrate this dependence of change of density on change of grain size, these data for the compacts were plotted as shown in figure 6. Sections of representative photographs have been included as part of this figure which shows the size and position of pores with different grain sizes. This curve shows that during a portion of the sintering cycle, density increases with increasing grain size, and when near maximum density is reached, grain size continues to increase with no appreciable increase in density. For specimens sintered below 1538°C (2800°F) for time periods in excess of 90 minutes, the density and the grain size of the specimens would be expected to follow the curve established by the specimens sintered at the higher temperatures. Initial particle size finer than that used in this investigation would probably cause this entire curve to be shifted to the left, resulting in maximum density being attained with a smaller final grain size.

This investigation shows that in addition to densification, grain growth occurs during the second stage of sintering described in reference 1. From figure 6, it is apparent that grain growth continues after densification is complete, and this continuation may be considered as a third stage in the sintering process. The sintering process for chromium carbide may therefore be described by a first stage during which the particles preserve much of their original shape and a substantial bond has formed between adjacent particles; a second stage during which densification occurs (pores reduce in size and spheroidize) accompanied by grain growth (n is 10) and; the third stage during which there is no appreciable change in density because pores are located

within the grains and grain growth is the predominant phenomena (n is 6). In order to prepare compacts with maximum density and minimum grain size, sintering must be terminated in the early portions of this third stage.

During this third stage of sintering, grain growth appears to obey the Arrhenius type equation

$$K = Ae^{-\frac{Q}{RT}} \quad (2)$$

where

K rate constant for sintering process (equation (1))

A constant

Q molal energy of activation, calories per mole

R gas constant (1.99 cal per mole/ $^{\circ}\text{K}$)

T absolute temperature, $^{\circ}\text{K}$

Thus

$$\ln K = n \ln D - \ln t = -\frac{Q}{RT} + \ln A \quad (3)$$

For a fixed grain size and a given value of n , the plot of $\ln t$ against $1/T$ should give a straight line of slope Q/R . It may be seen from figure 7 that this relation is valid for each range of temperature in which n is constant. Thus, in a certain time t_1 at absolute temperature T_1 and in time t_2 at a different absolute temperature T_2 (in the same range), a given grain size can be attained. The relation between these four quantities may be expressed as

$$\ln \frac{t_1}{t_2} = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

The values of Q obtained from figure 7 are shown in the following table:

Sintering stage	Reciprocal of slope	Grain size (microns)	Energy of activation, Q (cal/mole)
2	10	8.5	172,000
3	6	15.0	140,000

During the second stage of sintering (n is 10), the sintering process consists of the complex mechanisms of densification as well as grain growth. When n is 6, in the third stage of sintering, no appreciable densification takes place and the Q calculated may be interpreted as the activation energy for grain growth.

CONCLUSIONS

The investigation of the kinetics of sintering chromium carbide under pressure indicated that:

1. Densification (reduction in size and spheroidization of pores) is accompanied by grain growth during the second stage of sintering, and density and grain size appear to be interdependent during this portion of the sintering process.
2. Grain growth continues after densification is complete (when the pores are located within the grains) and this continuation may be considered as a third stage in the sintering process.
3. Grain growth follows the empirical equation $D^n = Kt$ where D is grain diameter, K is a rate constant, and t is sintering time. A change in n is associated with the second and third stages of sintering.
4. An activation energy for grain growth during the third stage of sintering of chromium carbide can be computed.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
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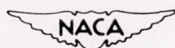


TABLE I - DENSITY AND GRAIN SIZE MEASUREMENTS OF CHROMIUM CARBIDE SPECIMENS

Sintering temperature		Sintering time, min									
		5		15		30		45		90	
(°C)	(°F)	Density (g/ml)	Grain size (microns)	Density (g/ml)	Grain size (microns)	Density (g/ml)	Grains size (microns)	Density (g/ml)	Grain size (microns)	Density (g/ml)	Grain size (microns)
1260	2300									4.80	
1371	2500	5.38	6.50	5.66	7.30	5.88	7.70	5.94	8.20	6.03	8.50
1426	2600	5.54	8.05	5.98	8.95	6.04	9.75	6.12	10.05	6.30	10.60
1482	2700	5.99	8.65	6.11	9.95	6.12	10.75	6.37	11.10	6.42	11.50
1538	2800	6.04	9.10	6.34	10.80	6.57	12.35	6.57	13.20	6.61	14.90
1593	2900	6.10	11.20	6.46	12.50	6.65	15.20	6.65	16.40	6.65	18.30
1648	3000	6.62	12.75	6.61	15.90	6.64	18.60	6.64	19.10	6.65	21.40

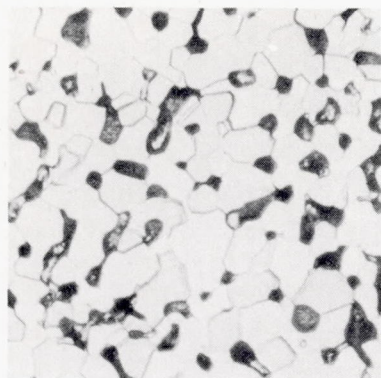
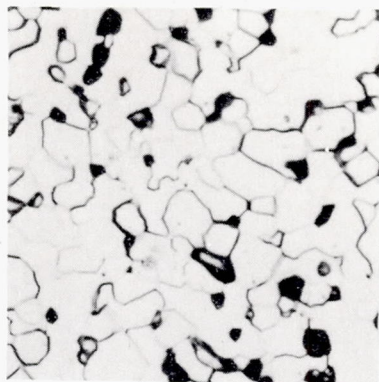
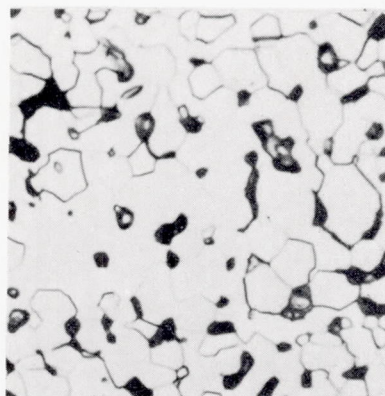
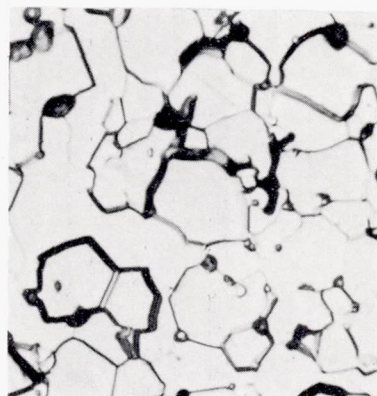
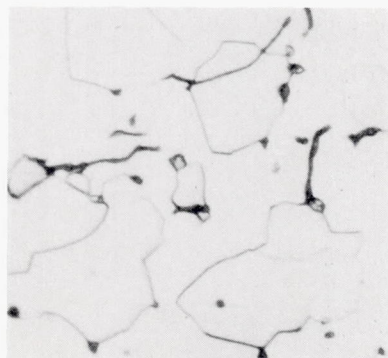
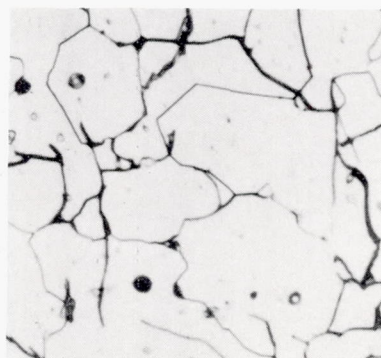
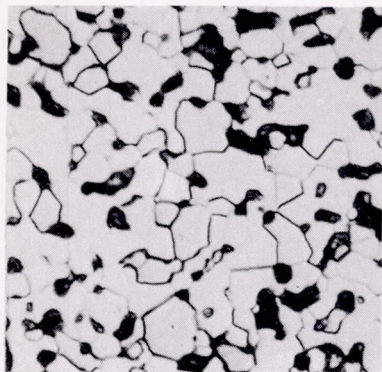
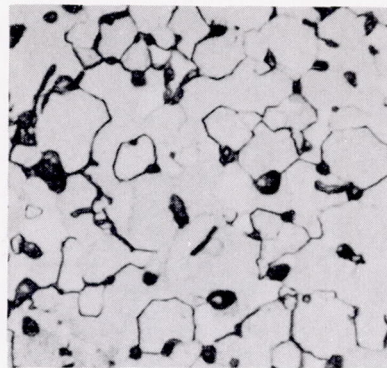
(a) 1371°C (2500°F).(b) 1426°C (2600°F).(c) 1482°C (2700°F).(d) 1538°C (2800°F).(e) 1593°C (2900°F).(f) 1648°C (3000°F).

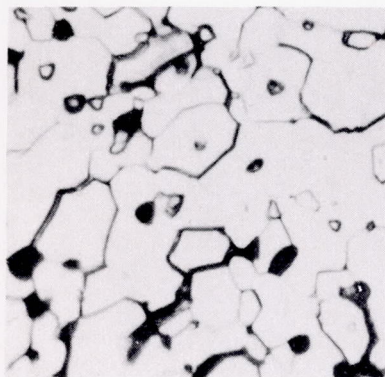
Figure 1. - Photomicrographs of specimens sintered at various temperatures for 90 minutes.
X1000.



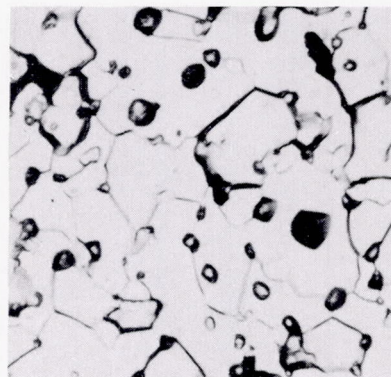
(a) 5 minutes.



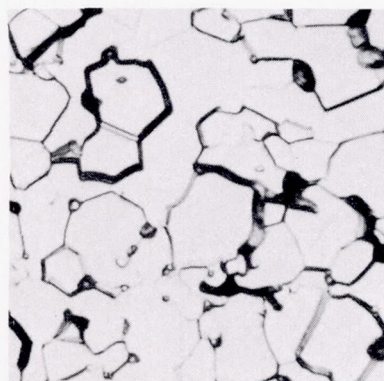
(b) 15 minutes.



(c) 30 minutes.



(d) 45 minutes.



(e) 90 minutes.

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Figure 2. - Photomicrographs of specimens sintered at 1538°C (2800°F) for various times.
X1000.

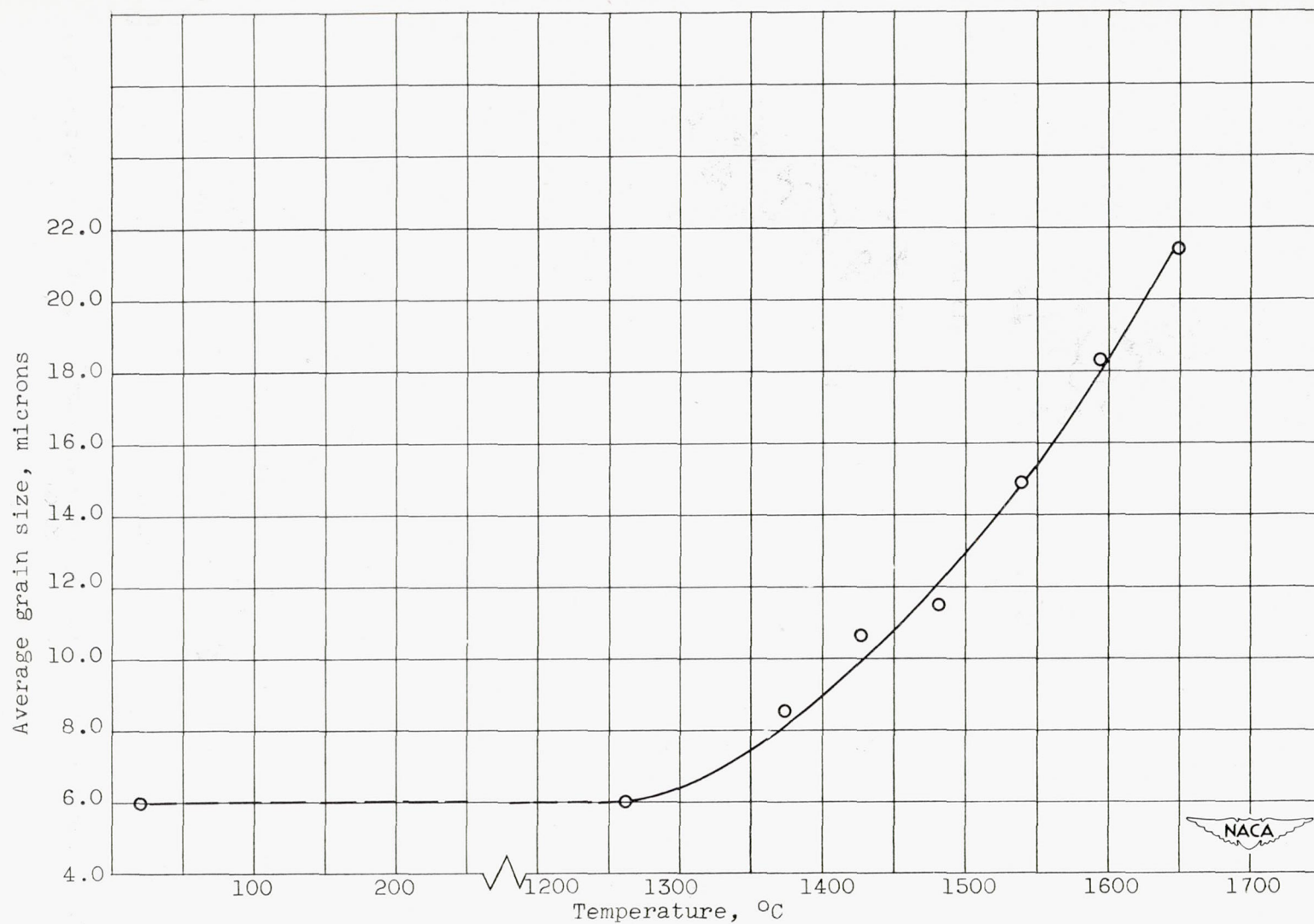


Figure 3. - Variation in average grain size of sintered chromium carbide with sintering temperature; time period of 90 minutes.

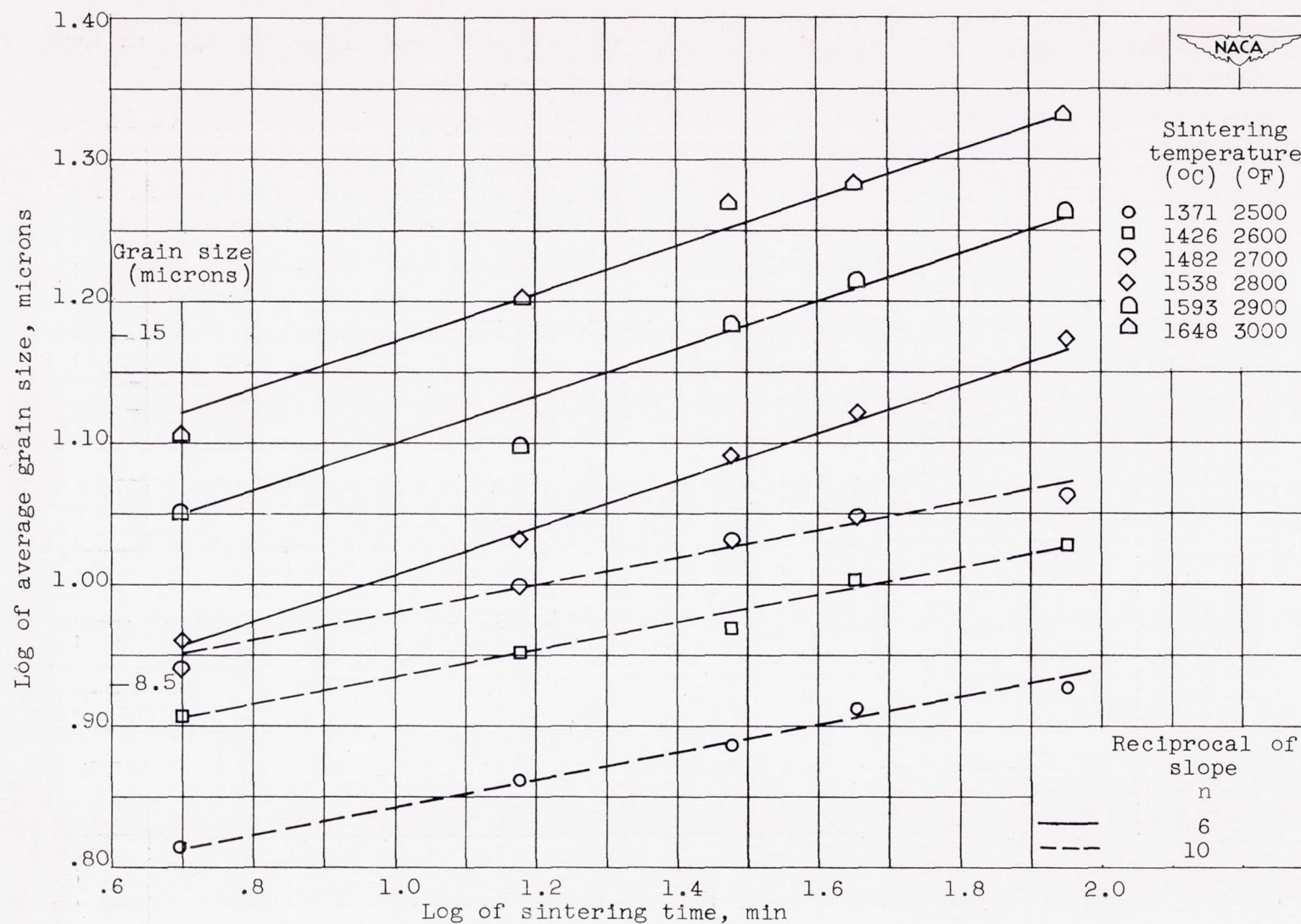


Figure 4. - Isothermal grain growth for sintered chromium carbide.

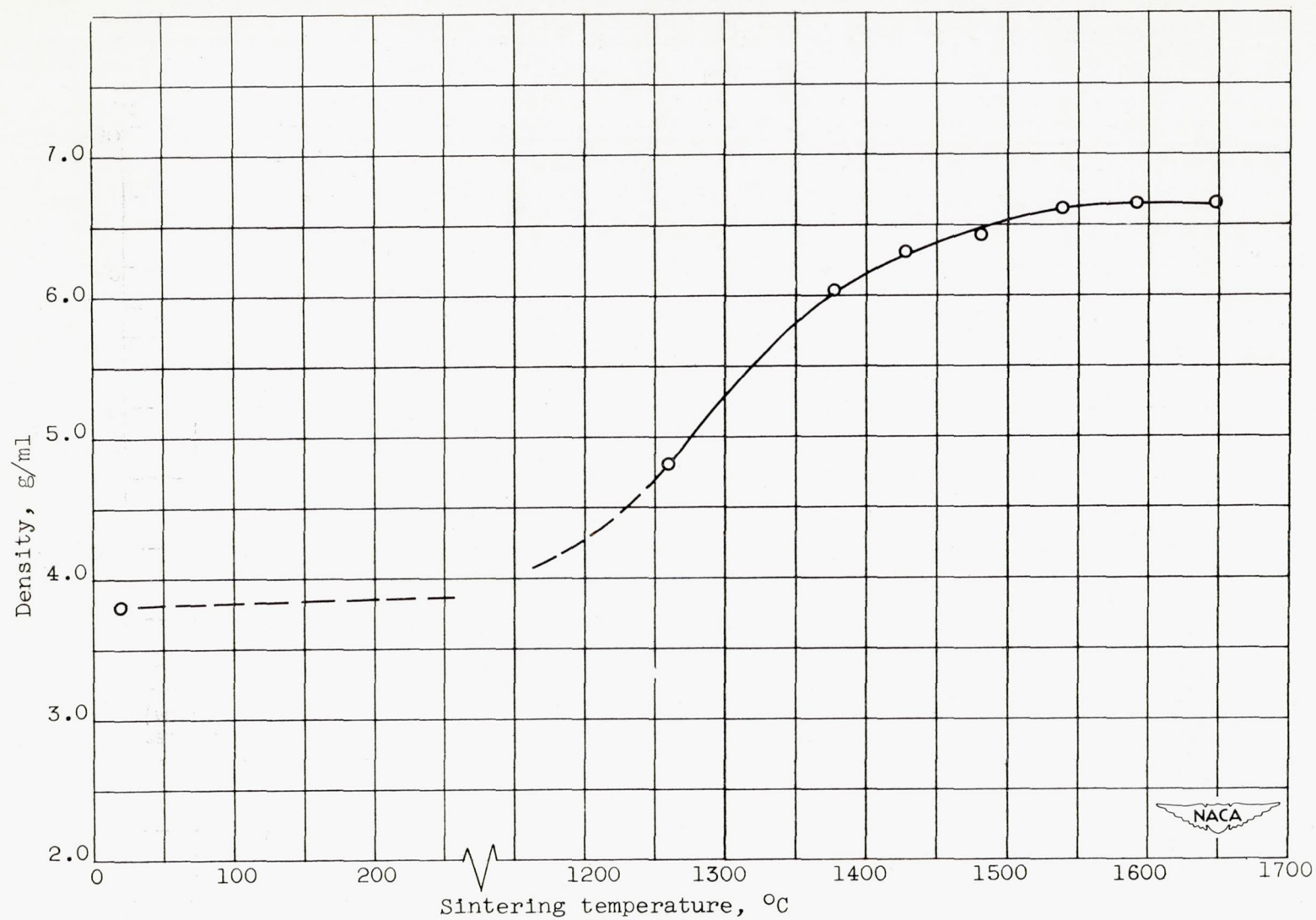


Figure 5. - Variation in density of sintered chromium carbide with sintering temperature for time period of 90 minutes.

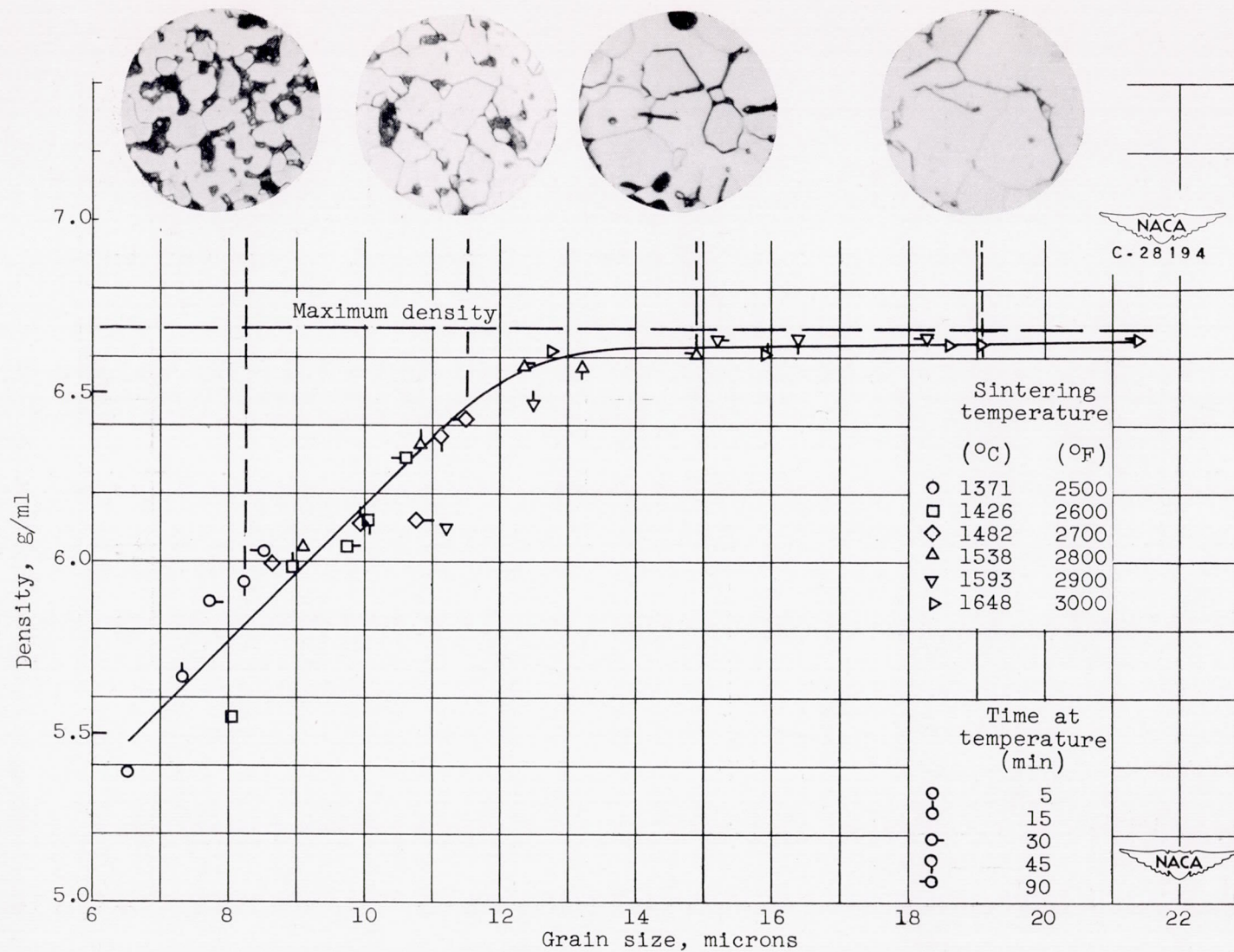


Figure 6. - Variation of density with grain size for specimens sintered at different temperatures and time periods.

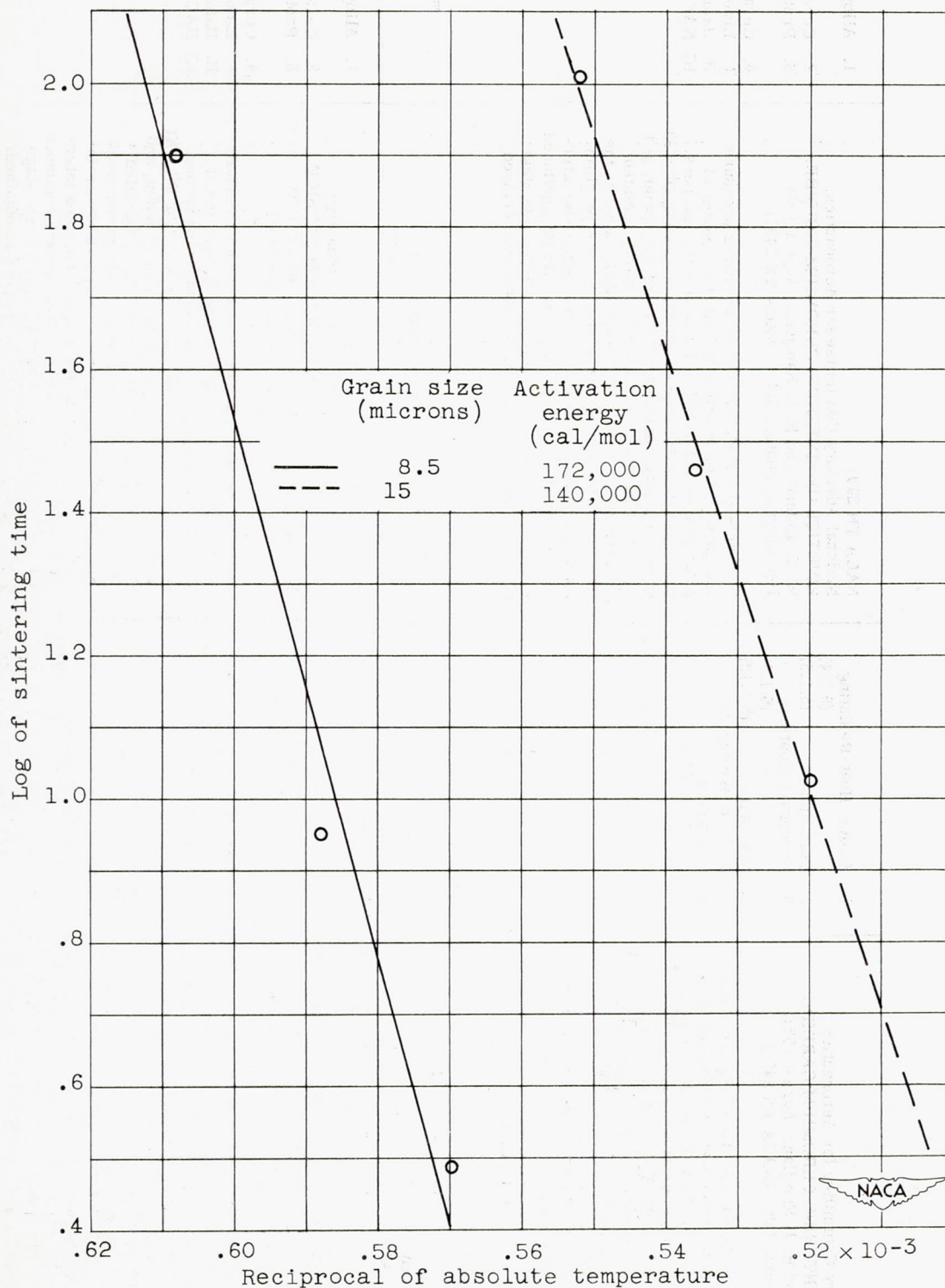


Figure 7. - Variation of sintering time to obtain average grain size of 8.5 and 15 microns with reciprocal of absolute sintering temperature.